

Monodispersed gold nanoparticles supported on γ -Al₂O₃ for enhancement of low-temperature catalytic oxidation of CO

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Abstract

Monodispersed nano-Au/ γ -Al₂O₃ catalysts for low-temperature oxidation of CO have been prepared via a modified colloidal deposition route, which involves the deposition of dodecanethiolate self-assembled monolayer (SAM)-protected gold nanoparticles (C₁₂ nano-Au) in hexane on γ -Al₂O₃ at room temperature. The diameter of the gold nanoparticles deposited on the support is 2.5 ± 0.8 nm after thermal treatment, and their valence states comprise both the metallic and oxidized states. It is found that the thermal treatment temperature affects significantly the catalytic activity of the catalysts in the processing steps. The catalyst treated at 190 °C exhibits considerably higher activity as compared to catalysts treated at 165 and 250 °C. A 2.0-wt.% nano-Au/ γ -Al₂O₃ catalyst treated at 190 °C for 15 h maintains the catalytic activity at nearly 100% CO oxidation for at least 800 h at 15 °C, at least 600 h at 0 °C, and even longer than 450 h at –5 °C. Evidently, the catalysts obtained using this preparation route show high catalytic activity, particularly at low temperatures, and a good long-term stability.

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1. Introduction

For a long time, gold has been considered to be one of the chemically inert and catalytically inactive metals due to its poor chemisorption of the bulk state. However, it has been widely proven that a gold catalyst exhibits very high catalytic activity towards low-temperature CO oxidation when the gold nanoparticles are smaller than approximately 4 nm and highly dispersed on the support [1]. Thus, since Haruta et al. discovered that the supported gold catalysts prepared by the co-precipitation method were very active for CO oxidation at temperatures below 0 °C, a variety of supported gold catalysts such as Au/TiO₂, Au/ γ -Al₂O₃, Au/Fe₂O₃ and Au/Co₃O₄ have been synthesized and applied in different application fields [2–11].

Many methods such as co-precipitation [2,3], colloidal deposition [12], laser vaporization [13], chemical vapor deposition (CVD) [14], organic gold-complex grafting [15],

deposition precipitation (DP) [16], impregnation [17], liquid-phase grafting [18], cation exchange [19] and amorphous metal alloy methods [20] have been used to prepare high-activity gold catalysts. Some of them involve many sophisticated apparatuses and a number of processing steps. Thus, in order to acquire efficient gold catalysts, novel preparation routes for obtaining finely monodispersed gold on metal oxides have recently been widely investigated. At present, monodispersed gold nanoparticles with sizes ranging from 2 to 4 nm were synthesized in a solution by different methods. Nonetheless, fabrication of monodispersed gold nanoparticles on metal oxides has been so far unsuccessful, mainly due to the requirement of high-temperature pretreatment of catalysts. In the traditional preparation methods such as the co-precipitation, DP and CVD methods, pretreatment is indispensable for enabling metal-support interaction [4,13,21]. Furthermore, the thermal treatment is thought to decompose the oxidized gold species in the precursor into metallic species to form small particles, which are postulated to be the active catalytic sites [4]. However, the treatment at high temperatures could cause the sintering of gold particles, which will lead to a significant

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decrease in the catalytic activity. Moreover, it has been reported that the partially oxidized gold species of catalysts are the most active sites for low-temperature CO oxidation [22]. Consequently, the choice of the treatment temperature (activation temperature) is very important and decreasing the treatment temperature is a key step for creating highly active gold catalysts.

Low-temperature CO oxidation of gold catalysts has been studied extensively over the past two decades. It is noteworthy that the catalytic performances of the gold catalysts generally increase with decreasing the particle size of the dispersed gold particles on the support [20,21]. The preparation method strongly influences the particle size. In the earlier literature, gold catalysts supported on γ -Al₂O₃ or α -Fe₂O₃ prepared by a conventional impregnation method exhibited little catalytic activity for CO oxidation, mainly due to low gold dispersion ($d > 10$ nm) [2,23]. Haruta et al. have showed that highly dispersed ($d < 5$ nm) gold catalysts can be prepared on various metal oxide supports using the traditional co-precipitation and DP methods [2–4]. In fact, some gold catalysts with high metal loading, such as 5 atom% Au/ α -Fe₂O₃, 10 atom% Au/NiO, exhibit high CO oxidation activity even at -70 °C [2]. However, these two traditional methods usually lead to formation of larger gold particles ($d > 7$ nm) on the Al₂O₃ support [24]. This is not beneficial to preparation of active catalysts. Recently, Comotti et al. [12] have reported that the Au/ γ -Al₂O₃ catalysts with high gold dispersion ($d < 5$ nm) are successfully prepared by the colloidal deposition method, which involves the deposition of preformed colloidal gold nanoparticles on the support. The major advantage of this method is that it offers precise control over the particle size before deposition on various supports. However, the majority of gold catalysts prepared by the above-described methods are usually thermally treated at higher temperatures (at or above 250 °C). As mentioned previously, high-temperature treatment induces the agglomeration of the gold nanoparticles on the support, which eventually influences the catalytic performance.

In this work, we report a modified colloidal deposition route for the preparation of monodispersed gold catalysts using prefabricated alkanethiolate SAM-protected gold nanoparticles in hexane colloidal solution as precursor. The thermal treatment of the catalysts is carried out at a lower temperature (190 °C). The aim of this work is to obtain highly active and stable catalysts for low-temperature CO oxidation by improving the preparation technique.

2. Experimental

2.1. Chemicals

Dodecanethiol (C₁₂S, $\geq 98\%$, Alfa Aesar), sodium borohydride (NaBH₄, 99%, Aldrich), γ -alumina (γ -Al₂O₃, $> 93\%$, 280–400 mesh) and all other reagents from standard sources were used as received. Water was purified using a Milli-Q water system.

2.2. Catalyst preparation

At present, there are many methods for the preparation of monolayer-protected gold nanoparticles [25–29]. One of the most popular methods for preparing monolayer-protected gold nanoparticles (≤ 5 nm) was a two-phase protocol described by Brust et al. [26], in which tetraoctylammonium bromide was used as phase transfer agent and toluene was used as solvent. Xu et al. [29] recently developed a method, which involved the use of tetrabutylammonium bromide as the phase transfer agent to transfer tetrachloroaurate (AuCl₄[−]) ions from aqueous saturated sodium chloride solution to tetrahydrofuran (THF). Because THF was easily dissolved in water, using aqueous saturated sodium chloride solution as the water phase could increase the density of water and separate the organic phase from the water phase to form a two-phase system. In this study, the route for preparing dodecanethiolate-SAM gold nanoparticles (C₁₂ nano-Au) is further modified by us based on Xu et al.'s and Brust et al.'s works, which is described as follows.

5 mL of an aqueous saturated sodium chloride solution containing 0.035 M hydrogen tetrachloroaurate (HAuCl₄) was added to 8 mL of THF solution containing 0.1 M tetrabutylammonium bromide. The two-phase mixture was vigorously stirred for 30 min. Subsequently, 12 mL of THF solution containing 0.0438 M dodecanethiol was quickly added to the two-phase mixture. After 10 min of stirring, 5 mL of freshly prepared aqueous saturated sodium chloride solution containing 0.42 M sodium borohydride was quickly added with vigorous stirring at room temperature, and a dark brown solution was immediately produced. After further stirring for 2 h, the dark brown phase was separated with a separatory funnel and evaporated to 1 mL in a rotary evaporator. The black slush was suspended in 100 mL of absolute ethanol, briefly sonicated to ensure the complete dissolution of by-products, left for 24 h, collected on a glass filtration frit, and cleaned several times using ultrapure water and ethanol. The product of C₁₂ nano-Au was dissolved in *n*-hexane. The hexane C₁₂ nano-Au colloidal solution was used as the impregnant in the preparation of the nano-Au/ γ -Al₂O₃ catalyst.

γ -Al₂O₃ powder was calcined in air at 550 °C for 4 h. The hexane C₁₂ nano-Au colloidal solution was prepared by dissolving C₁₂ nano-Au containing 1.6 mg of Au in 1 mL of hexane. In order to obtain nano-Au/ γ -Al₂O₃ catalysts with different gold loadings, different amounts of the above hexane gold colloidal solution (1.6 mg/mL) were added to a fixed amount of γ -Al₂O₃. The final gold loading in the catalysts was determined by atomic absorption spectroscopy (AAS). In a typical experiment for preparation of a 2.0-wt.% gold catalyst, 12.8 mL of 1.6 mg/mL hexane C₁₂ nano-Au colloidal solution was added portionwise to 1 g of γ -Al₂O₃ by following process in order to make the C₁₂ nano-Au highly dispersed on γ -Al₂O₃. The hexane gold colloidal solution was added dropwise to the γ -Al₂O₃ powder under continuously stirring until the latter became saturated, as evidenced by initial appearance of tiny amount of excess of hexane gold colloidal solution, and then the hexane was removed through volatilization at room temperature. After the

removal of the hexane, more hexane gold colloidal solution could be added to the γ - Al_2O_3 powder. Then, the above process was repeated until all of the 12.8 mL of hexane gold colloidal solution was added.

2.3. Instruments

High-resolution transmission electron microscopic (HRTEM) measurement was performed using a TECNAI F30 electron microscope (FEI, USA) operating at 300 kV. Low-resolution TEM measurement was carried out using a JEM-2100HC electron microscope (JEOL, Japan) operating at 200 kV. To obtain a suitable sample for TEM characterization, the C_{12} nano-Au was dissolved in hexane and the catalyst powder was dispersed in ethanol by ultrasonication. One drop of a ~ 1 mg/mL solution, containing the C_{12} nano-Au or the nano-Au/ γ - Al_2O_3 catalyst, was deposited onto standard carbon-coated (200–300 Å) Formvar films on copper grids (400 mesh); the films were dried in air for at least 45 min. The size distributions of the gold nanoparticles were measured from enlarged TEM image photographs of 150 individual nanoparticle images.

Quantum 2000 X-ray photoelectron spectroscopy (XPS) spectrometer (Physical Electronics, USA) with monochromatic Al K α (1486.6 eV) radiation was used to determine the binding energy and valence states of gold in the materials. The binding energy scale was corrected for surface charging by considering the C1s peak of contaminant carbon as a reference at 285.0 eV.

Thermogravimetric analysis (TGA) of the C_{12} nano-Au was conducted using a STA 409 PC thermal analyzer (Netzsch, Germany) under Ar atmosphere. The sample was heated from 30 to 400 °C at a heating rate of 10 °C/min.

The gold loading in the catalyst was determined by a SOLAAR M6 atomic absorption spectrometer (AAS, Thermo Electron, England).

2.4. Catalytic activity measurement for CO oxidation

Catalytic activity measurements were carried out in a fixed-bed flow U-shaped glass reactor filled with 200 mg of the nano-Au/ γ - Al_2O_3 catalyst. A gas mixture containing 2.0-vol.% CO balanced with air (absolute humidity: $4.04 \times 10^{-3} \text{ g m}^{-3}$) was passed through the catalyst bed at the flow rates—100 mL min $^{-1}$

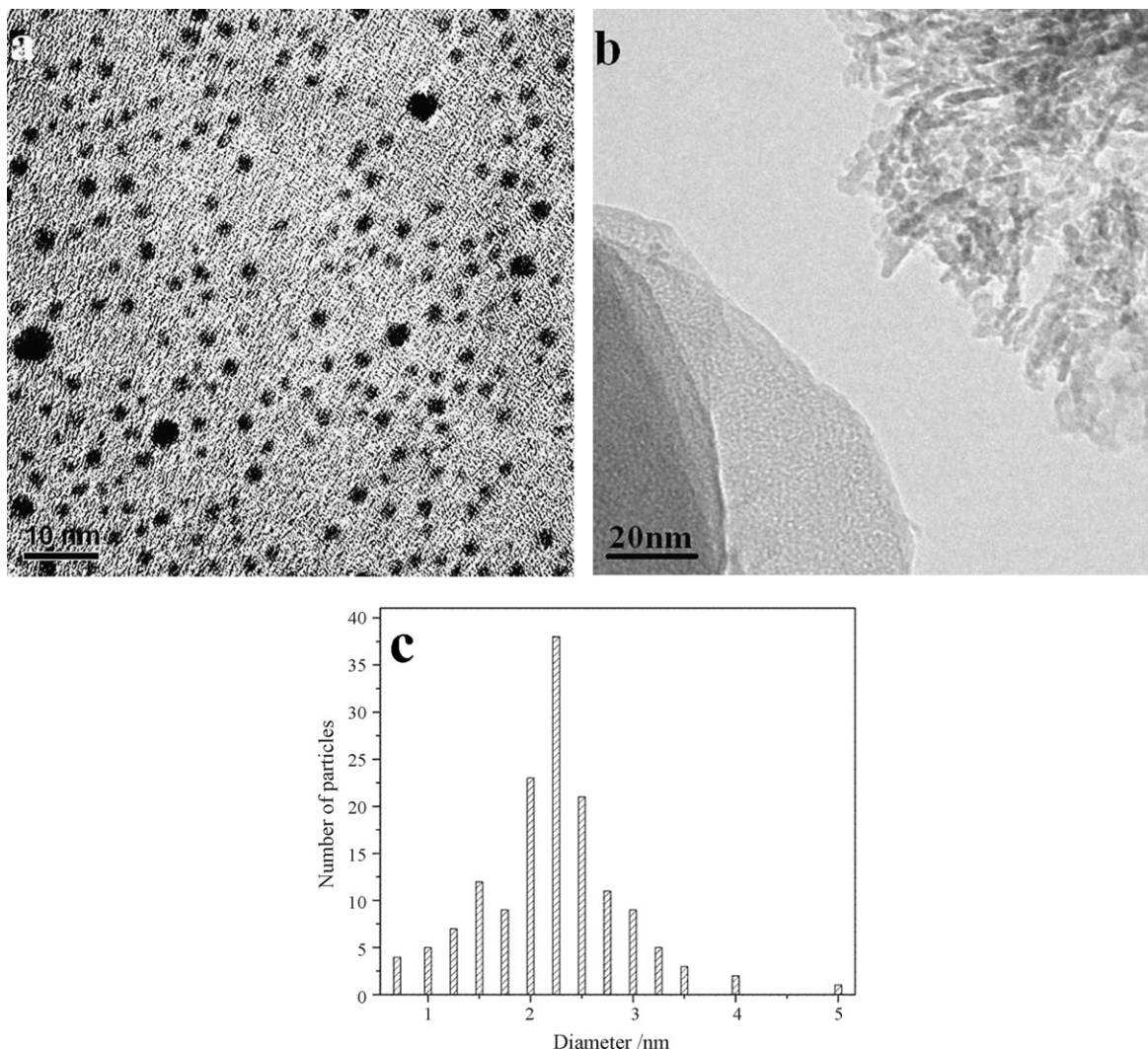


Fig. 1. TEM images of (a) C_{12} nano-Au and (b) commercial γ - Al_2O_3 , and (c) size distribution histogram of C_{12} nano-Au.

(SV = 30,000 mL h⁻¹ g⁻¹) and 233 mL min⁻¹ (SV = 70,000 mL h⁻¹ g⁻¹). The gas analyses were performed by a gas chromatograph equipped with a molecular sieve column using a thermal conductivity detector. The reaction activity was indicated by the lowest temperature at which 100% conversion (denoted by T_L) of CO was obtained under the reaction conditions. Before each activity measurement, the catalyst was thermally treated at 190 °C for 15 h in the reaction gas at a flow rate of 50 mL min⁻¹ (SV = 15,000 mL h⁻¹ g⁻¹) in order to activate it.

3. Results and discussion

3.1. Characterization of nano-Au/ γ -Al₂O₃

The shape and, in particular, the size of gold nanoparticles which are deposited on the support affect the catalytic activity of

catalysts [1,4,21]. The TEM images of C₁₂ nano-Au and commercial γ -Al₂O₃ are shown in Fig. 1. The gold nanoparticles have a spherical shape and an average size of 2.2 ± 0.5 nm. The commercial γ -Al₂O₃ is rod-shaped, and its diameter and length are typically 2–3 and 7–30 nm, respectively. Some of the short γ -Al₂O₃ rods gather to form a film. Fig. 2 shows TEM images of the 2.0-wt.% gold catalysts for three stages: as prepared, after thermal treatment at 190 °C and after 450 h of reaction. The size distribution histograms of the gold particles which are deposited on the support corresponding to Fig. 2a–c are presented in Fig. 2d. The shape of the gold nanoparticles deposited on the γ -Al₂O₃ support, appearing as dark spots, is almost spherical in all the TEM images. There is no apparent difference in the shape in the three stages. A relatively narrow size range of approximately 2–3 nm is observed for the gold particles in the three stages of the catalyst, as shown in Fig. 2d, confirming that the gold particles

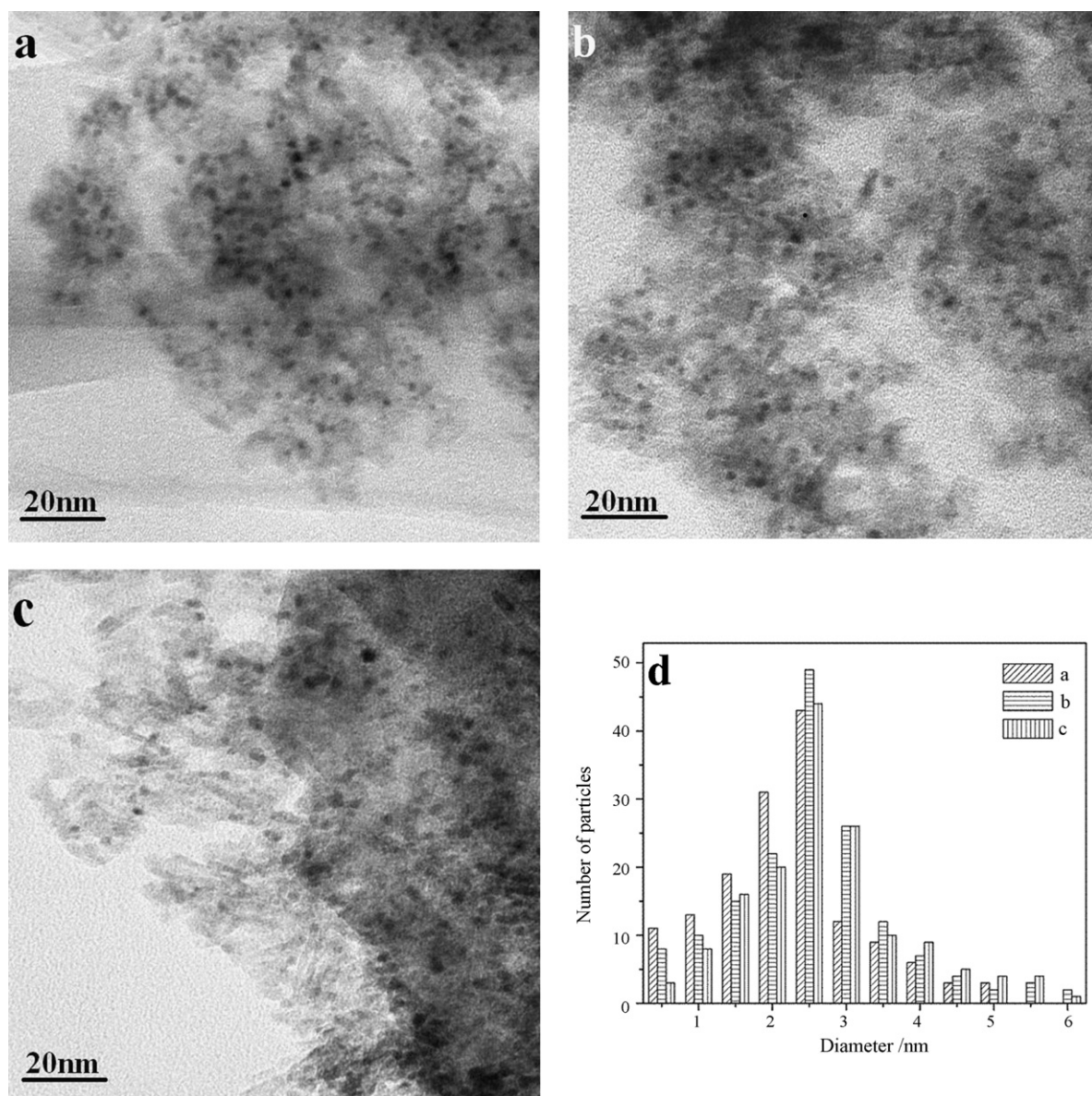


Fig. 2. TEM images of the 2.0-wt.% nano-Au/ γ -Al₂O₃ catalyst. (a) As prepared, (b) after thermal treatment at 190 °C in a reaction gas containing 2.0 vol.% CO balanced with air at a flow rate of 50 mL min⁻¹ (SV = 15,000 mL h⁻¹ g⁻¹), (c) after 450 h of reaction, and (d) size distribution histogram of gold nanoparticles.

are monodispersed on the support. The average sizes of the gold particles are 2.3 ± 0.7 (as prepared), 2.5 ± 0.8 (after thermal treatment at 190°C) and 2.5 ± 0.9 nm (after 450 h of reaction). There is no aggregation of the nanoparticles even after 450 h of reaction. For the as-prepared catalyst, as expected, the average size of the gold nanoparticles is almost the same as that of the gold nanoparticles in the gold colloidal solution because the gold particles are protected by the SAM, as shown in Figs. 2a, d and 1c. In addition, it can be found from Figs. 2b–d and 1c that the average sizes of the gold particles on the support are slightly larger than those of the gold particles in the gold colloidal solution whenever the catalyst is thermally treated at 190°C or has been active for 450 h. This indicates that no significant size change occurs during the thermal treatment and reaction. The TEM images of catalysts with different metal loadings after 450 h of reaction are shown in Fig. 3. The size distributions of the

gold particles are almost identical for all the samples. The average sizes and standard deviations are 2.4 ± 0.7 (1.62 wt.%), 2.5 ± 0.9 (1.92 wt.%) and 2.5 ± 1.1 nm (2.83 wt.%). The average sizes of the gold nanoparticles on the $\gamma\text{-Al}_2\text{O}_3$ support slightly increase in comparison with those of the gold nanoparticles in the gold colloidal solution.

In order to obtain a closer insight into the interaction between gold particles and their supports, XPS measurements were carried out. The results of the 2.0-wt.% nano-Au/ $\gamma\text{-Al}_2\text{O}_3$ catalysts in the three stages (a: as prepared; b: after thermal treatment at 190°C and c: after 450 h of reaction; these are marked as Samples 1, 2 and 3, respectively, for convenience) are shown in Fig. 4 and summarized in Table 1. The XPS spectra of the samples are fitted with two components. The $4f_{7/2}$ binding energies (BEs) of standard gold compounds were reported in the literature (Au^0 : 84.0 eV, $\text{Au}^{\text{III}}\text{-O}$: 85.5–86.3 eV) [22]. Samples 1,

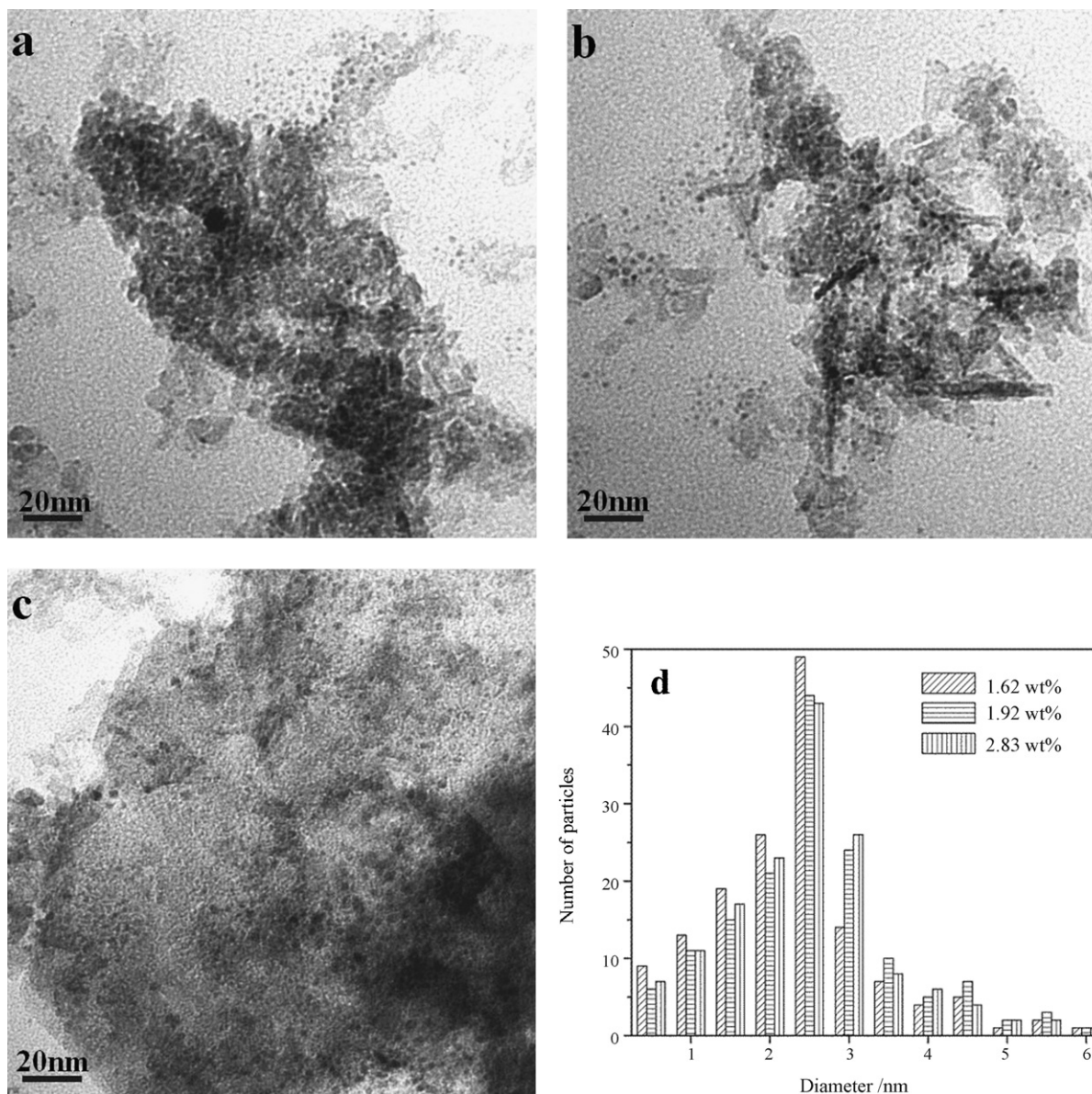


Fig. 3. TEM images of the nano-Au/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with different metal loading after 450 h of reaction. (a) 1.62 wt.%, (b) 1.92 wt.%, (c) 2.83 wt.%, and (d) size distribution histogram of gold nanoparticles.

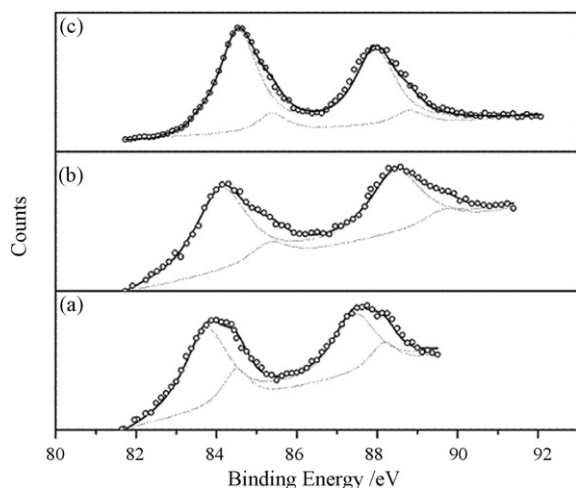


Fig. 4. XPS spectra of Au 4f of the 2.0-wt.% nano-Au/ γ -Al₂O₃ catalysts: (a) as prepared; (b) after thermal treatment at 190 °C; (c) after 450 h of reaction.

2 and 3 have lower Au 4f_{7/2} BEs of 83.8, 83.5 and 83.9 eV, respectively, as compared to the literature value of 84.0 eV; the higher BEs of samples 1, 2 and 3 are 84.5, 84.4 and 84.8 eV, respectively, which are 0.5, 0.4 and 0.8 eV higher than the BE of 84.0 eV. On the basis of a comparison with the BEs of a standard gold compound, the component corresponding to the lower BE is attributed to gold in the metallic state, and the second component corresponding to the higher BE, which is present in a minor amount, is assigned to gold in a partially oxidized state. The partially oxidized state of C₁₂ nano-Au in sample 1 is attributed to Au–S bonds. Because some of the Au–S bonds of sample 2 are broken during the thermal treatment at 190 °C, the partially oxidized state of gold mainly originates from the thermal treatment. A negative shift of 0.5 eV for the lower BE peak of Au 4f_{7/2} of sample 2 at 83.5 eV can be possibly attributed to the strong metal-support interaction [13]. After 450 h of reaction, the lower BE peak of the metallic state gold of sample 3 at 83.9 eV is close to that of the metallic state of the standard gold compound, and furthermore its intensity increases slightly.

3.2. Evaluation of catalytic performances

In order to induce a metal-support interaction or to obtain the active phase of gold, the majority of gold catalysts prepared by chemical methods are usually thermally treated in air, reducing

Table 1
Au 4f_{7/2} binding energy and relative proportions of the various gold species

Sample	Au 4f _{7/2} (eV)	Au species (%)
1	83.8	Au ⁰ (79)
	84.5	Au ^{III} -O (21)
2	83.5	Au ⁰ (86)
	84.4	Au ^{III} -O (14)
3	83.9	Au ⁰ (89)
	84.8	Au ^{III} -O (11)

Sample 1: as prepared; sample 2: after thermal treatment at 190 °C and sample 3: after 450 h of reaction.

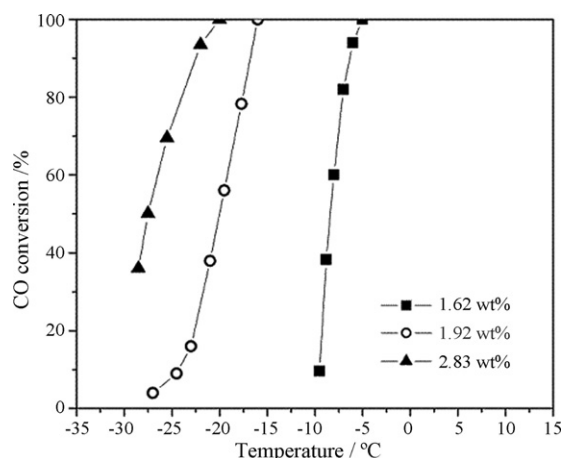


Fig. 5. Conversion efficiencies of nano-Au/ γ -Al₂O₃ catalysts with different metal loading for CO oxidation as a function of reaction temperatures.

gas atmospheres or oxidizing gas atmospheres to produce active catalysts [4,13]. In the present study, all the performance evaluations are performed using the activated nano-Au/ γ -Al₂O₃ catalysts.

Fig. 5 displays the conversion efficiencies for CO oxidation as a function of the temperature. As observed, all the nano-Au/ γ -Al₂O₃ catalysts function at a relatively low-temperature for 100% CO conversion under the same reaction conditions. The lowest temperatures at which 100% CO conversion was obtained for the nano-Au/ γ -Al₂O₃ catalysts with 1.62, 1.92 and 2.83 wt.% metal loadings, are –5, –16 and –20 °C, respectively. This indicates that increasing the metal loading of the catalysts will be beneficial in increasing the low-temperature catalytic activity. Furthermore, the catalyst with only 2–3 wt.% gold loading exhibits a relatively high-activity.

The thermogravimetric analysis (TGA) curve for the C₁₂ nano-Au is shown in Fig. 6. The mass decrease starts at approximately 180 °C and a 25% mass loss occurs at 300 °C, which is almost consistent with the expectation based on a model calculation of the mass decrease percentage of the dodecanethiolate monolayer shell [28]. Based on the TGA result, three different temperatures, namely, 165, 190 and 250 °C, are chosen

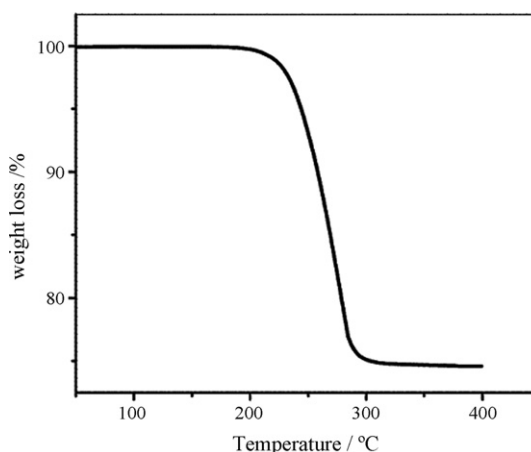


Fig. 6. A TGA curve of dodecanethiolate-protected Au nanoparticles.

Table 2

Treatment temperature and activity of the 2.0 wt.% nano-Au/ γ -Al₂O₃ catalysts indicated by the lowest 100% CO conversion temperature

Sample	Treatment temperature (°C)	T_L (°C)
1	165	160
2	190	−16
3	250	120

as the thermal treatment temperatures. The desorption of thiolate does not occur at 165 °C and just begins at 190 °C. When the temperature increases to 250 °C, a large amount of thiolate is rapidly removed. Thus, in order to study the effect of thermal treatment on the catalytic activity of catalysts, the 2.0-wt.% nano-Au/ γ -Al₂O₃ catalysts were calcined for 15 h at 165, 190 and 250 °C, respectively, and subsequently their catalytic activities were tested. The results are summarized in Table 2. When thermally treated at 190 °C, the nano-Au/ γ -Al₂O₃ catalyst exhibits a relatively high low-temperature catalytic activity, but when thermally treated at 165 and 250 °C, its low-temperature catalytic activities are very low. The possible reasons for this phenomenon are considered. As mentioned above, the mass decrease of the C₁₂ nano-Au just starts at 190 °C. Further, the desorption of thiolate molecules is considerably reduced during the thermal treatment process at this temperature, which is beneficial in maintaining the size and monodispersity of the gold nanoparticles. The TEM image (Fig. 2b) of the catalyst that is thermally treated at 190 °C demonstrates that the gold particles which are deposited on γ -Al₂O₃ are not agglomerated. When the nano-Au/ γ -Al₂O₃ catalyst is thermally treated at 165 °C, no mass decrease occurs for C₁₂ nano-Au, which indicates that the gold particles are still protected by the thiolate at the temperature. Thus, the catalytic activity of the catalyst is very low, probably due to the inhibitory effect of the protecting agent. When the nano-Au/ γ -Al₂O₃ catalyst is thermally treated at 250 °C, the thiolate molecules are rapidly removed at this temperature. At the same time, this process easily causes the localized aggregation of the nanoparticles. Thus, the sizes of the gold nanoparticles which are deposited on γ -Al₂O₃ are increased (~15 nm in diameter), as shown in Fig. 7, and this increase leads to lower catalytic activity of the catalyst. Consequently, it can be concluded that the thermal treatment temperature has an important effect on the catalytic activities for CO oxidation, particularly at low-temperatures.

To investigate the long-term stability of the catalyst, stability tests were carried out under different reaction conditions. Fig. 8a shows the conversion efficiencies of CO as a function of the duration time at different temperatures at a flow rate of 100 mL min^{−1} (SV = 30,000 mL h^{−1} g^{−1}). The 2.0-wt.% nano-Au/ γ -Al₂O₃ catalyst after the thermal treatment at 190 °C for 15 h is so stable that it can maintain the catalytic activity at nearly 100% CO oxidation for at least 800 h at 15 °C and 600 h at 0 °C. Even when the temperature decreases to −5 °C, it can retain the catalytic activity for nearly 100% conversion of CO for longer than 450 h. Fig. 8b shows the conversion efficiency of CO as a function of time at a flow rate of 233 mL min^{−1} (SV = 70,000 mL h^{−1} g^{−1}). The result shows that a 3.5-wt.% nano-Au/ γ -Al₂O₃ catalyst can maintain nearly 100% CO conversion for 1500 h (at 20 °C) at the flow rate of

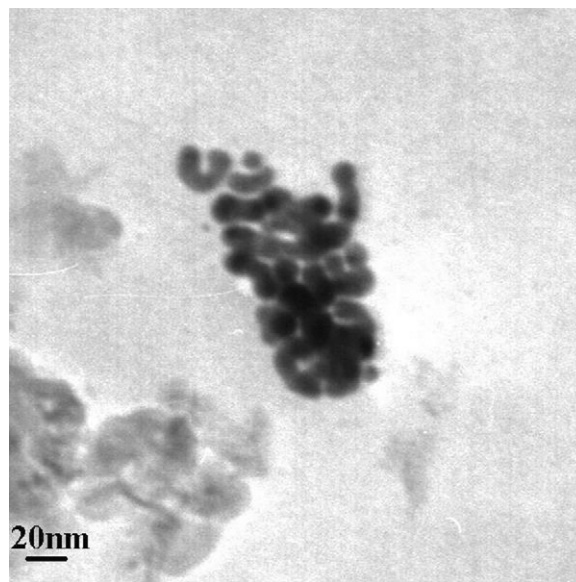


Fig. 7. A TEM image of dropcast film of the 2.0-wt.% nano-Au/ γ -Al₂O₃ catalyst after thermal treatment at 250 °C.

233 mL min^{−1}. Then, the decrease in activity is observed. The above results of the performance evaluations of the nano-Au/ γ -Al₂O₃ catalysts show that highly active and stable catalysts for CO oxidation, particularly at low-temperatures, can be prepared by improving the preparation technique employed in this work.

As noted in Section 1, the use of size-tunable prefabricated gold nanoparticles for preparation of active Au/ γ -Al₂O₃ catalysts has been reported in the literature. In a typical preparation, the γ -Al₂O₃ support has been impregnated with an aqueous colloidal gold solution followed by filtration, washing and drying. It has

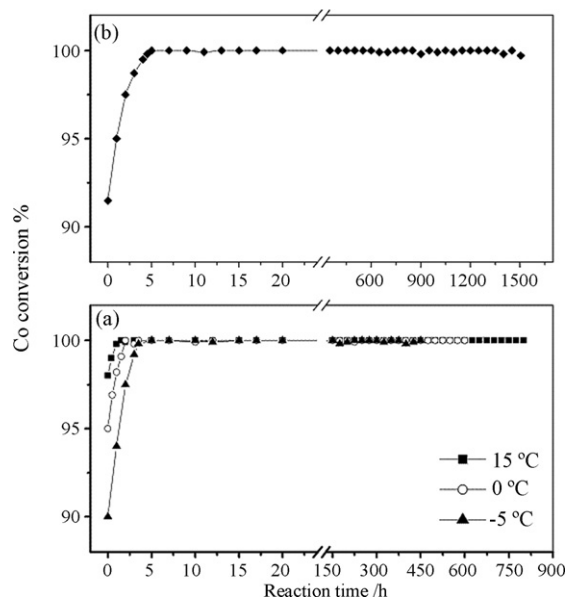


Fig. 8. CO catalytic oxidation on the nano-Au/ γ -Al₂O₃ catalyst in a fixed-bed flow reactor as a function of reaction time in a reaction gas containing 2.0-vol.% CO balanced with air (a) at different temperature at a flow rate of 100 mL min^{−1} (SV = 30,000 mL h^{−1} g^{−1}, gold loading: 2.0 wt.%) and (b) at 20 °C and at a flow rate of 233 mL min^{−1} (SV = 70,000 mL h^{−1} g^{−1}, gold loading: 3.5 wt.%).

been found that a 1-wt.% Au/ γ -Al₂O₃ catalyst exhibits high catalytic activity for 100% CO conversion at approximately 0 °C in a gas mixture of 1% CO in air and at a flow rate of 67 mL min⁻¹ [12]. In this work, we develop a different colloidal deposition route to prepare the nano-Au/ γ -Al₂O₃ catalysts that show high catalytic activity and stability towards low-temperature CO oxidation in a reaction gas containing a relatively high concentration of CO (2.0-vol.% CO) and at a high flow rate (100 mL min⁻¹). The 2-wt.% Au/ γ -Al₂O₃ catalyst prepared can completely convert CO to CO₂ at -16 °C and maintain the catalytic activity at nearly 100% CO conversion for even longer than 450 h at -5 °C. Compared to the reported colloidal deposition method, the approach employed in this work has three key features in the deposition process and the thermal treatment as follows. First, the gold particles are deposited on the support by using hexane solution containing the particles as the impregnant. The rapid evaporation of volatile hexane enables the gold particles to be rapidly in situ deposited and highly dispersed on the support. Second, the hexane gold colloidal solution is added dropwise to the support under stirring until that tiny amount of the hexane gold colloidal solution is initially observed on the support surface. This is a key step for enhancing particle dispersion on the support. Third, before the activity measurement, the gold catalyst is thermally treated at 190 °C in the reaction gas for 15 h in this work, while the typical thermal treatment temperature is usually above 250 °C in the reported literatures [2,4,12,21]. Treatment at lower-temperatures contributes to avoiding the agglomeration of the gold nanoparticles and keeps the particles monodispersed on the support. Catalytic tests in Table 2 clearly show that the nano-Au/ γ -Al₂O₃ catalyst calcined at 190 °C exhibits evidently higher activity than that calcined at 250 °C. TEM images (Figs. 1a, c and 2a–d) show that there are no noticeable differences in the morphology and core size of the gold particles during deposition and the thermal treatment, even after the reaction proceeds for 450 h, and moreover, the particles are highly dispersed on the γ -Al₂O₃ at all times. This is beneficial in maintaining high catalytic activity. In addition, the XPS results in Table 1 reveal that strong metal-support interaction, which is one of critical factors for high-activity, can be produced after the thermal treatment at 190 °C.

4. Conclusions

In summary, in this work, a series of monodispersed nano-Au/ γ -Al₂O₃ catalysts have been prepared by a modified colloidal deposition route. TEM investigations show that the majority of the gold particles dispersed on the support are in a narrow size range of 2–3 nm, and the average size and monodispersity change only slightly during the thermal treatment and reaction. The influence of the treatment temperature on the catalytic activity has been studied. The nano-Au/ γ -Al₂O₃ catalyst calcined at 190 °C exhibits 100% conversion of CO at temperatures below -5 °C, whereas the catalysts calcined at 165 and 250 °C exhibit 100% conversion at temperatures above 120 °C. In addition, the long-term stability of the gold catalyst has been investigated. The 2.0-wt.% nano-Au/ γ -Al₂O₃ catalyst can be successfully used for 450 h at -5 °C without any loss of

activity. In principle, by using the preparation route, other oxide-supported metal catalysts with monodispersed particles can also be synthesized at room temperature.

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